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Oxidation of Electrostatically Paired Porphyrin and Phthalocyanine

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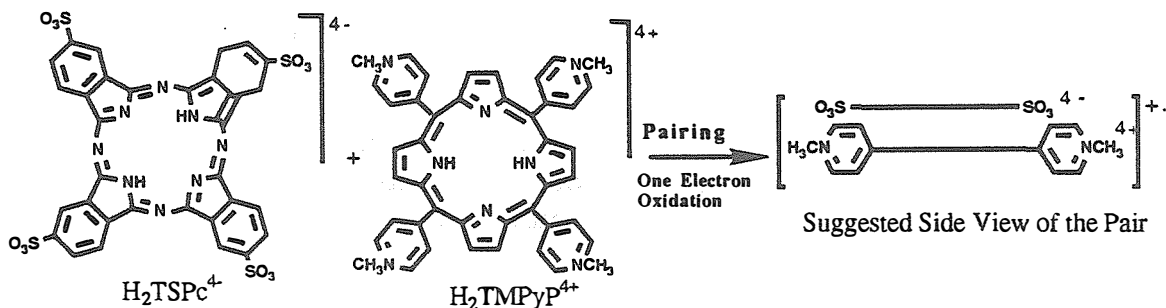
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OXIDATION OF ELECTROSTATICALLY PAIRED PORPHYRIN AND PHTHALOCYANINE

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The primary donor in the photosynthetic reaction center of bacteria is formed by two bacteriochlorophyll *b* molecules known as the special pair. Our synthetic model system for the special pair consists of electrostatically paired porphyrin and phthalocyanine molecules. The goals of current work are to confirm the single electron oxidation and to characterize the radical species formed in the oxidation process. We have prepared the free base salts tetra-(*N*-methyl-4-pyridyl)porphyrin hexafluorophosphate $\text{H}_2\text{TMPyP}(\text{PF}_6)_4$ and tetraphenyl-phosphonium tetrasulfatophthalocyanine $(\text{Ph}_4\text{P})_4\text{H}_2\text{TSPc}$ which are soluble in propylene carbonate. An electrostatically paired cofacial complex is expected to form between these two free-base molecules. This free-base derivative is also expected to undergo one-electron oxidation.



Using rigorously dry solvent allowed $\text{H}_2\text{TMPyP}^{4+}$ and $\text{H}_2\text{TSPc}^{4-}$ molecules to form a complex. The stoichiometry of the complex was determined to be 1:1 and the pair formation constant, K_1 , was estimated to be $1.36 \pm .01 \times 10^8$. The dependence of K_1 on ionic strength was studied at various concentrations of tetra-*n*-butylammonium tetrafluoroborate Bu_4NBF_4 . With increasing ionic strength K_1 decreases. This dependence is expected to obey the Debye-Hückel limiting law. Phthalocyanine and the complex were oxidized at 0.425 and 0.320 V vs SCE (aq), respectively. From the evaluation of the measured potential difference between paired and unpaired phthalocyanine, the equilibrium constant for the formation of the singly oxidized pair was determined to be 2.0×10^6 .